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Polymer-Carbon Nanotube Composites

A Literature Review

Trisha A. Huber

Defence R&D Canada – Atlantic

Technical Memorandum

DRDC Atlantic TM 2004-091

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Abstract

Carbon nanotubes were first discovered in 1991, and quickly became the focus of much research activity, due to their exceptional electrical, mechanical, and thermal properties. The extraordinary properties arise from the unique tubular structure; the nanotubes may be envisioned as rolled up graphene sheets that are on the order of a nanometer in diameter, and microns in length, resulting in high aspect ratios (length/diameter). In addition to the many applications of pure carbon nanotubes (gas storage, sensors, electronic devices, electron microscope tips, and electron emission devices), there are also a number of applications in which the nanotubes are dispersed in a polymeric matrix, such as electromagnetic shielding, antistatic coatings, high-strength low-density corrosion-resistant components, and lightweight energy storage. The presence of small amounts of nanotubes in an insulating polymeric matrix has been found to improve the mechanical properties as well as render the composite electrically conductive, thus polymer-carbon nanotube composites are of interest primarily for their mechanical and electrical properties. When the matrix polymer is also electrically conductive, in many cases the composite exhibits enhanced electrical properties. This technical memorandum is a survey of current literature on both insulating and conductive polymer – carbon nanotube composites.

Résumé

On a découvert les nanotubes de carbone en 1991 et ils sont rapidement devenus l'objet de plusieurs activités de recherche en raison de leurs exceptionnelles propriétés électriques, mécaniques et thermiques. Ces propriétés extraordinaires découlent de leur unique structure tubulaire; les nanotubes se présentent comme des feuilles de graphite enroulées en cylindres, d'un diamètre de l'ordre du nanomètre pour quelques microns de longueur, résultant en un rapport longueur/diamètre élevé. En plus des nombreuses applications des nanotubes de carbone pur (entreposage de gaz, capteurs, dispositifs électroniques, pointes de microscopes électroniques et dispositifs d'émission électronique), il existe également plusieurs applications, telles que la protection électromagnétique, les revêtements antistatiques, les composantes rigides, à faible densité et résistantes à la corrosion et les dispositifs légers de stockage d'énergie, utilisant des nanotubes dispersés dans une matrice polymérique. L'ajout de petites quantités de nanotubes dans une matrice polymérique isolante améliore les propriétés mécaniques du composite et le rend conducteur d'électricité; les composites polymériques et de nanotubes de carbone sont très intéressants, surtout en raison de leurs propriétés mécaniques et électriques. Lorsque la matrice polymérique est déjà conductrice d'électricité, le composite possèdera souvent de meilleures propriétés électriques. Le présent mémoire technique est une recension des écrits scientifiques récents sur les composites de nanotubes de carbone et de polymères isolants et conducteurs.

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Executive summary

Introduction

Carbon nanotubes, discovered just over a decade ago, have enjoyed unprecedented attention from the scientific community due to the extraordinary properties that arise as a result of their unique structure. Carbon nanotubes are an allotrope of carbon and may be envisioned as tubes formed by rolled up graphitic sheets. The nanotubes form either as single walled nanotubes (SWNTs), or multi walled nanotubes (MWNTs), depending on the reaction conditions. They are extremely strong and thermally conductive. Their electrical properties are interesting, as the nature of the electrical conductivity depends on the chirality, or twist, of each tube; the electrical conductivity ranges from semiconducting to metallic, in nature. There are a number of reports in the literature of composites of carbon nanotubes and polymeric matrices; the results indicate that even small amounts of nanotubes (< 5 wt %) can have a significant influence on the electrical and mechanical properties of the composite. This technical memorandum gives a brief overview of carbon nanotubes, their applications, and a summary of the recent literature of polymer – nanotube composites.

Significance (including military significance, if any)

There are a number of military applications involving carbon nanotubes and nanotube-polymer composites, including electromagnetic shielding and absorption, frequency-selective coatings, antistatic devices, high-strength low-density corrosion-resistant components, lightweight energy storage, electronic devices, transducers, sensors (chemical and pressure), and nonlinear materials (for electro-optical warfare).

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Sommaire

Introduction

Les nanotubes de carbone, dont la découverte remonte à près de dix ans, ont suscité une attention sans précédent de la part du milieu scientifique, en raison des propriétés extraordinaires découlant de leur structure unique. Les nanotubes de carbone sont des allotropes du carbone se présentant comme des feuilles de graphite enroulées en cylindres. Selon les conditions de réaction, leurs parois sont simples ou multiples. Les nanotubes sont extrêmement résistants et sont d'excellents conducteurs de chaleur. Ils possèdent des propriétés électriques intéressantes, car la nature de leur conductivité dépend de la chiralité, ou du sens de la torsion, de chaque tube. Leur conductivité électrique peut se situer entre celle d'un semi-conducteur et celle d'un métal. Il existe plusieurs écrits scientifiques sur des composites de matrices polymériques et de nanotubes de carbone qui concluent que, même de petites quantités de nanotubes (inférieures à 5 % en masse) peuvent modifier beaucoup les propriétés électriques et mécaniques du composite. Le présent mémoire technique donne un aperçu des nanotubes de carbone et de leurs applications, et résume les écrits récents sur les composites de polymères et de nanotubes.

Importance (y compris la portée militaire)

Il existe un bon nombre d'applications militaires des nanotubes de carbone et des composites de polymères et de nanotubes, notamment la protection contre les ondes électromagnétiques et leur absorption; les revêtements dont les propriétés varient avec la fréquence; les dispositifs antistatiques; les composants haute résistance, à faible densité et résistant à la corrosion; les dispositifs légers de stockage d'énergie; les transducteurs, les capteurs (chimiques et de pression) et les matériaux non linéaires (pour la guerre électro-optique).

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1. Carbon Nanotubes

1.1 Introduction

In 1991, Sumio Iijima noticed novel structures in the byproduct soot created during fullerene production by electric arc-discharge.[1] Investigation revealed the tubular nature of these interesting structures, now known as carbon nanotubes, which have likely existed for years, but remained undiscovered up to this point. A carbon nanotube may be described as a graphene sheet rolled up to form a tube, with half-fullerene caps, for closed tubes. The caps are fairly reactive due to curvature strain, and are readily destroyed during processing, yielding open tubes.[2] Nanotubes are formed in a range of diameters and may be single-walled or multi-walled, depending on the reaction conditions. The single-walled variety exist as a bundle made up of strands, like a rope, in which each strand is a single-walled nanotube (SWNT); each bundle contains typically 10 – 50 strands and is 5 – 20 nm in diameter.[3] The diameter of SWNTs is on the order of a nanometer (~ 1.4 nm), and the intertube spacing within the bundle has been determined to be ~ 0.3 nm, at closest approach.[3] Multi-walled nanotubes (MWNT) are comprised of several graphene sheets rolled up, resulting in concentric tubes with successively larger radii. Multi-walled nanotubes also aggregate, due to significant van der Waals forces. The diameter of MWNTs is typically 10 – 20 nm, and the interlayer spacing has been determined to be ~ 0.34 nm).[3]

Carbon nanotubes range in electrical conductivity from metallic conductors to semiconductors; the electronic properties depend on the diameter and the helicity, or chirality (degree of twist of the tube), that are determined by the chiral vector, $\mathbf{C}_h$, which connects crystallographically equivalent sites (see Figure 1),[3]

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \tag{1}$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors of the hexagonal lattice, and the indices, n and m, are integers ($0 \leq |m| \leq n$). The chiral vector is most often expressed as (n, m), and the chiral angle, θ, is defined as the angle between $\mathbf{C}_h$ and $\mathbf{a}_1$. The chiral vector in Figure 1, describes a (6, 3) nanotube, which results when the graphene sheet is rolled such that the head and the tail coincide. The axis of the nanotube is orthogonal to the chiral vector. The chiral angle, θ, (therefore chirality) and diameter, d_t, of a nanotube are readily calculated from n and m, as follows,[3]

$$\cos\theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}} \tag{2}$$

$$d_t = \frac{C_h}{\pi} = \frac{a_{C\text{-}C}\sqrt{3}}{\pi}\sqrt{n^2 + m^2 + nm} \tag{3}$$

where $a_{C\text{-}C}$ is the nearest neighbour distance in graphite (1.42 Å).

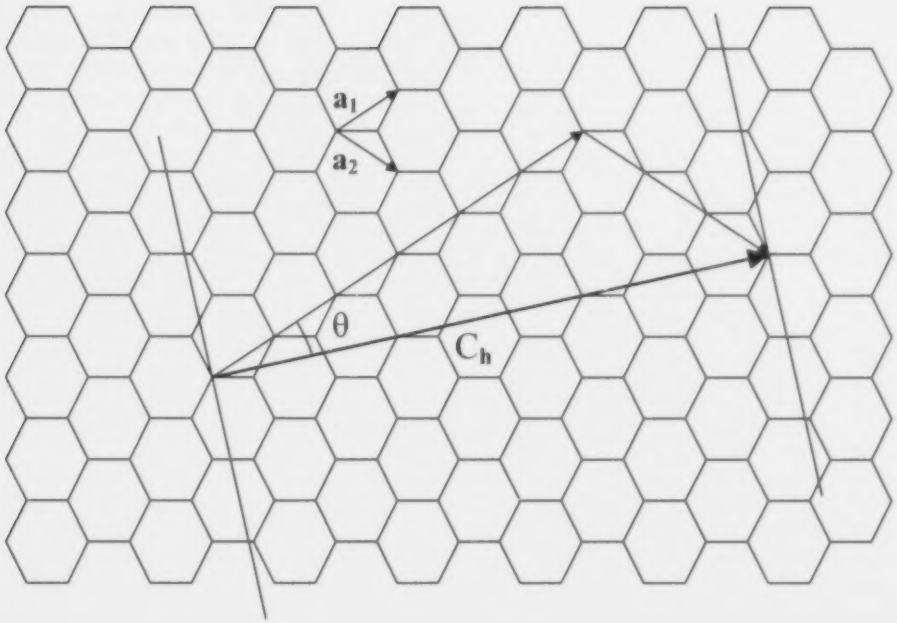

Figure 1. *Carbon Nanotube Chiral Vector for a (6, 3) tube*

The chiral angle can take on any value between 0° and 30°. Nanotubes with a chiral angle of 0° correspond to (n, 0), and are known as zigzag tubes; those with a chiral angle of 30° correspond to (n, n), and are known as armchair tubes. Both zigzag and armchair tubes are considered to have no chirality, whereas all other (n, m) tubes are chiral (non-superimposable mirror images).[3]

As mentioned previously, the electronic properties depend on the diameter and the chirality of the nanotubes. In fact, whether the nanotube is metallic or semiconducting can be readily determined by the (n, m) indices. All armchair tubes, (n, n), exhibit metallic conductivity; zigzag tubes, (n, 0), where n is a multiple of 3, exhibit metallic conductivity; in the case where n – m is a multiple of 3, the tubes are metallic; all other (n, m) tubes are semiconducting. Statistically, given a random distribution of nanotubes, approximately ⅓ are metallic and ⅔ are semiconducting.[3] A successful method to selectively produce metallic or semiconducting tubes has not yet been developed, however, methods designed to separate them from each other are actively being pursued.[4-6] In addition, effective means of sorting tubes according to diameter are also being investigated.[7]

The serendipitous discovery of carbon nanotubes was immediately followed by a flurry of research activity. Since 1991, a multitude of papers describing various production methods

and means of characterizing this new allotrope of carbon, have appeared in the literature. There have also been a number of investigations into the formation mechanism, mechanical, thermal, and electrical properties, as well as the chemistry and potential uses, and composites of nanotubes. Other aspects of nanotubes under investigation include the joining of dissimilar tubes[8] and their electrical properties.[9] In addition, scientists are currently investigating the preparation of nanotubes that contain fullerenes (known as pea pods),[10] or those in which nitrogen[11] or boron[12,13] is incorporated into the tube. There are also a number of groups utilizing various methods to organize and manipulate nanotubes.[14-18] As well, there is evidence presented indicating the formation of MWNTs having a scroll structure, in which layers arise from one continuous sheet rolled around itself.[19]

1.2 Properties

The excitement of their discovery is not simply due to the interesting structure of the nanotubes, but their phenomenal properties as well. Carbon nanotubes exhibit an exceptional combination of electrical, mechanical, and thermal properties,[20] primarily as a result of their highly ordered structure and extensive conjugated π-system. Metallic nanotubes can be as conductive as copper, and semi-conducting tubes conduct as well as silicon,[20] if not better due to higher charge carrier mobility.[21,22] Conductivity measurements of an aligned nanotube film indicate electrical anisotropy, as expected, with the conduction in the direction parallel to the tube axis being greater than perpendicular to it;[23] inter-tube transport is limited by contact resistance. Conduction along a metallic nanotube (even weakly disordered) is proposed to be ballistic (no scattering),[24,25] enabling such tubes to carry a high current with little heating. The presence of defects results in scattering, thereby reducing the conductivity. For MWNTs, inter-tube coupling is weak, thus it is proposed that the outer tube carries almost all of the electrical current,[26,27] although some speculate that several layers take part in charge transport. SWNTs generally exhibit fewer defects than MWNTs, and low temperature conductivity measurements on SWNTs indicate coherence of electronic states over a distance of more than a hundred nanometers; thus SWNTs may be considered to be quantum wires.[28] An interesting feature of carbon nanotubes is that they can be doped by the intercalation of alkali metals and halogens. Intercalation results in charge transfer, yielding n-doped nanotubes in the case of alkali metals (electron donors), and p-doped nanotubes in the case of halogen intercalates (electron acceptors).[29,30] Doped nanotubes have been observed to exhibit conductivity at least one order of magnitude greater than undoped nanotubes.[28,31,32]

Carbon nanotubes exhibit exceptional mechanical properties, in that they are very strong and resilient at the same time. It is claimed that they are a hundred times stronger than steel,[33] exhibiting a Young's modulus as high as one TPa,[33,34] as well as being able to buckle reversibly, without fracturing.[35]

In addition to their superior electrical and mechanical properties, carbon nanotubes are also thermally conductive,[25,36] exhibit magnetic anisotropy,[37] and possess large surface area[28] and low density.[28] The thermal conductivity of a MWNT at room temperature has been measured to be greater than 3000 W/m·K, exceeding that of diamond and graphite (2000 W/ m·K).[25] Nanotubes in a suspension have been found to respond to the application of a magnetic field by aligning themselves parallel to the applied field, as observed by SEM.[37] These results indicate the presence of magnetic anisotropy, with the susceptibility parallel to the tube axis

being larger than that perpendicular to the tube axis. Due to their nano-scale size, carbon nanotubes possess extremely large surface areas; BET (Brunauer-Emmett-Teller) measurements on MWNTs yield surface areas between 10 and 20 m^2/g, which is higher than graphite, but lower than activated porous carbon.[28] Furthermore, nanotubes are superior to metals for applications where low density ($\rho_{SWNT} = \sim 0.6$ g/cm^3, $\rho_{MWNT} = 1 - 2$ g/cm^3)[28] and corrosion-resistance are critical.

Despite their mechanical strength, carbon nanotubes are not indestructible. There is evidence that prolonged sonication can damage the nanotubes, reducing them to carbon nanofibres.[38] In addition, ball-milling has been shown to shorten MWNTs.[39] Furthermore, residual catalyst particles have been known to affect their stability; bright light from a camera flash has been known to ignite SWNTs, as a result of oxidation of residual iron particles.[40] A similar phenomenon was observed when an unpurified sample of SWNTs was exposed to a high power microwave source (2.45 GHz); the same experiment performed on purified tubes was much less dramatic, confirming the catalyst as the cause.[41]

1.3 Synthesis and Purification

Early synthetic methods for carbon nanotube production involved either electric arc-discharge or laser ablation, both of which use a high purity graphite rod as the carbon source. In the arc-discharge method, a voltage is applied across two graphite rods as electrodes. Carbon from the anode vapourizes and condenses on the cathode. In the laser ablation method, a laser vapourizes a graphite rod in a high temperature oven; a flow of argon carries the carbon vapour to a water-cooled collector upon which the carbon condenses. In both methods, the condensate contains nanotubes, amongst other forms of carbon. Both arc-discharge and laser ablation yield MWNTs, however, when the graphite target also contains catalyst particles, SWNTs are produced.[33] These methods are not amenable for industrial scale production, as a continuous process is not possible, and the amount of product is generally limited by the amount of graphite target used, although efforts are underway to overcome these limitations.[42-45]

Gas-phase methods have been developed, and are superior to arc-discharge and laser ablation in that they can operate as a continuous process, hence more suitable for commercial production. In addition, the process is generally more controllable, resulting in higher purity nanotubes. Chemical vapour deposition (CVD) is a process in which a hydrocarbon gas undergoes pyrolysis on a heated catalyst-coated surface. The HiPco process is similar, except uses high-pressure carbon monoxide as the carbon source. In addition to the conventional thermal CVD process, which produces random bundles of nanotubes, variations to the catalyst configuration and/or fine tuning of the reaction conditions results in the production of aligned arrays of nanotubes.[28,46-57] Unlike the nanotubes prepared in the bulk state, which are entangled, aligned nanotubes are useful for a number of applications (such as flat panel displays); as aligned nanotubes undergo deaggregation by the application of shear forces far more easily,[58] they are also good starting materials for the preparation of composites in which dispersion in polymeric matrices is required. Most aligned nanotubes are formed perpendicular to the substrate surface, however horizontal alignment can also be accomplished.[55] Variations on the thermal CVD method, such plasma enhanced CVD (PECVD), hot wire CVD (HWCVD)[59] or hot filament-assisted CVD (HFCVD),[45] rapid

thermal CVD (RTCVD),[60] microwave plasma CVD (MPCVD),[49] and floating catalyst techniques[52,61] have led to improvements in product controllability, yield, and cost.

Other aspects of nanotube synthesis currently under scrutiny include study of the growth mechanism,[60,62,63] attempts to control the diameter,[23,47,48,64-67] processes which yield very long nanotubes,[55,61,68] optimization of the catalyst composition[69] or other synthetic parameters,[70,71] and improvements in purity.[72] A major area of focus is the production of nanotubes at selected sites on a substrate (micropatterning).[51,53,73-79] Other areas of interest include the selective production of double-walled nanotubes (DWNTs),[80] and producing nanotubes that span two substrates.[81,82] There has also been a report of producing nanotubes which are aligned in several directions simultaneously.[83] Other synthetic methods are under investigation, such as a solvothermal route, in which reactants are heated at low to medium heat in solution in a sealed autoclave,[84,85] a solid state metathesis process,[86] a hydrothermal process which produces MWNTs from amorphous carbon,[87] and low temperature processes.[88]

Byproducts of nanotube production include amorphous carbon, carbon nanoparticles, and catalyst residues. Although many advances have been made in terms of scaling up the synthesis, a number of obstacles exist that relate to the purification of nanotubes. Purification is not trivial, as any treatment designed to remove metal catalyst particles and amorphous carbon can often result in functionalization of the tubes and/or the introduction of defects into the structure of the nanotubes. The most commonly used purification methods include oxidation (acid[89] or gas[90]), filtration,[91,92] or chromatography.[93-95] Less common methods include capillary electrophoresis,[96] and ultrasonication in the presence of inorganic nanoparticles.[97] Hydrothermal treatment has also been found to be effective in purification of SWNTs.[98] Many researchers employ a multi-step process to purify carbon nanotubes.

The most prevalent method, acid oxidation, generally oxidizes metals and carbon impurities, but can also functionalize the surface of the nanotubes. Depending on the strength of the acid or acid mixture, the damage to the nanotubes ranges from functionalization of defects extant from the growth process, to more severe damage such as the introduction and oxidation of additional defect sites, which can result in cutting of the tubes.[99] In addition to functionalization and tube cutting, acid oxidation has also been found to degrade SWNTs into MWNTs and onion-like carbon structures upon refluxing nitric acid treatment.[100] The use of a mild acid, such as dilute hydrochloric acid, has been found to react only with the end caps, which are more reactive due to curvature strain.[101]

A process known as annealing, which involves heating in an inert atmosphere[89] or under vacuum,[89,102,103] eliminates some of the structural defects, such as surface functionalization (resulting from acid treatment), and can also oxidize residual catalyst particles.[104] Heating SWNTs in air has also found to be effective in eliminating amorphous carbon, due to the relative thermal stability of the nanotubes.[105-107]

1.4 Characterization

Carbon nanotubes are usually characterized by electron microscopy, Raman scattering spectroscopy, and absorption spectroscopy. Both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) yield information regarding diameter distribution

and presence of impurities (amorphous carbon and residual catalyst particles), however the information is only qualitative. Scanning tunnelling microscopy (STM) images clearly show the hexagonal lattice, so much so that the chirality of the tube is visible;[108,109] this method effectively probes wave functions at various energies.[109] STM also yields information about the electronic density of states (DOS); consistence has been achieved between calculated DOS and measured DOS.[110] Figure 2 illustrates the calculated electronic DOS for a (9, 0) (metallic) nanotube and a (10, 0) (semiconducting) nanotube (the dotted line corresponds to the calculated density of states for a graphene sheet). The electronic nature of the nanotubes is evident by the DOS at the Fermi energy (0 eV); nonzero for the metallic tube, and zero for the semiconducting tube. In addition, the calculated DOS also reveal spikes, known as van Hove singularities, which exist as a result of the one-dimensional quantum confinement of the electrons.[3,111,112]

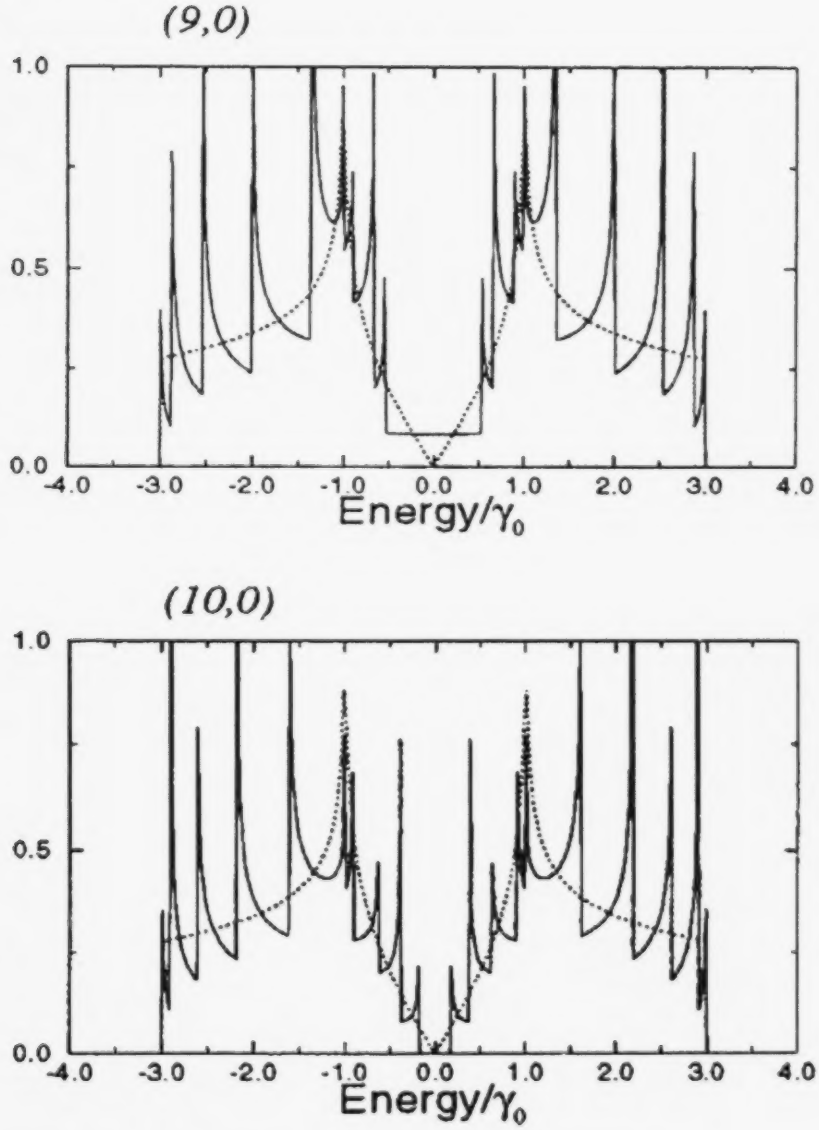

Figure 2. *Calculated Electronic DOS for a (9, 0) and a (10, 0) Nanotube.*

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It has been determined that the band gap is inversely proportional to the diameter, d_t. The band gap for semiconducting tubes, E^S_{gap}, may be estimated using equation (4), and that for metallic tubes, E^M_{gap}, may be estimated using equation (5);

$$E^S_{gap} = \frac{2\gamma_o a_{C\text{-}C}}{d_t} \tag{4}$$

and

$$E^M_{gap} = \frac{6\gamma_o a_{C\text{-}C}}{d_t} \tag{5}$$

where γ_o denotes the tight-binding overlap energy (2.45 eV), and $a_{C\text{-}C}$ denotes the nearest neighbour C-C distance (~ 1.42 Å).[9,113] As an example of the magnitude of the band gap, a semiconducting nanotube with a diameter of 1.4 nm has a band gap of ~ 0.5 eV.

Raman spectroscopy is useful for characterizing nanotubes, especially SWNTs. There are three regions of relatively intense peaks: the radial breathing mode (RBM) is found at low wavenumber (~ 150 – 300 cm^{-1}); the D-band (disorder-induced) (~ 1350 cm^{-1}) arises from the presence of amorphous carbon, and is generally used as an indicator of the purity; and the G-band (~ 1500 – 1600 cm^{-1}), the shape of which depends on the conducting nature of the nanotubes.[114] The RBM frequency has been found to be inversely proportional to the diameter according to

$$d(nm) = \frac{x}{\omega_{RBM}(cm^{-1})} \tag{6}$$

where x varies from 224 to 248 (depending on whether x is based on theory, or a combination of experiment and theory).[90,115,116] The D* band (disorder-induced overtone) (~ 2600 cm^{-1}) has also been used in the investigation of interaction between SWNTs and a polymer matrix[117] or other molecules.[118] The D* band is sensitive to strain as a result of breathing mode restriction.

Although Raman scattering is generally weak, a phenomenon known as resonant Raman scattering occurs with carbon nanotubes. When the Raman laser excitation energy is in resonance with the energy gap between pairs of van Hove singularities (valence → conducting, for example $v_1 \rightarrow c_1$, see Figure 3), the Raman scattering is enhanced, and thus much more intense. Figure 3 also illustrates the relationship between nanotube size (diameter) and band gap; the numerical values correspond to the band gap in eV, and the inverse relationship is evident. Tuning the laser excitation frequency to be in resonance with the energy separation between the van Hove singularities allows the determination of Raman spectra for specific nanotubes.[119] The transition energy between the van Hove singularities can be measured by absorption spectroscopy in the visible to near infrared (NIR) region of the electromagnetic spectrum; liquid suspensions of SWNTs typically exhibit broad asymmetric bands corresponding to the first intraband transition of a metallic tube, and the first and second intraband transition of a semi-conducting tube.[120] These bands are found to shift to higher energy as the diameter decreases, as predicted by theory.[121]

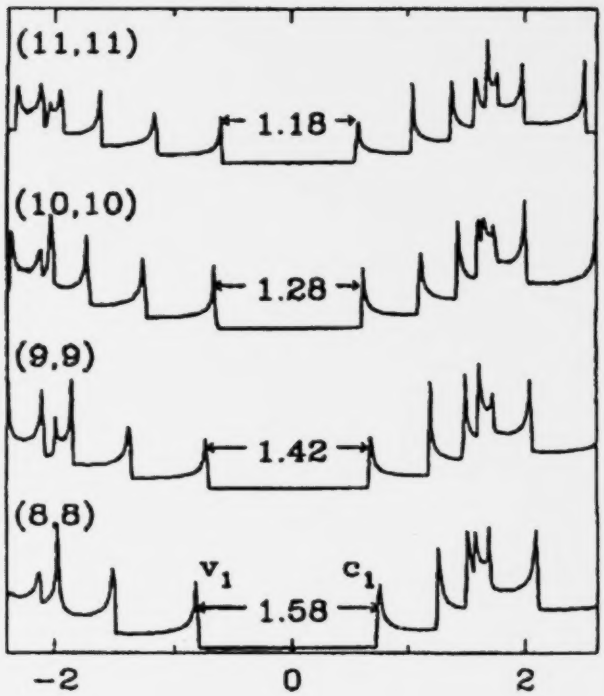

Figure 3. *Calculated Electronic DOS Illustrating the Nanotube Size and Band Gap Relationship for a Series of Armchair Nanotubes.*

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1.5 Applications

There is a wide range of applications, both potential and realized, for carbon nanotubes, from small-scale electronic devices to reinforcing filler. The state of the nanotubes (i.e. MWNTS or SWNTs, aligned or random, single tube, fibres, or bulk quantities, pure or dispersed in a matrix or electrospun into a fibre) is dictated by the application requirements. The ability of the nanotubes to be fabricated or processed into the required state illustrates their versatility.

Single nanotubes may comprise small-scale devices, such as transistors,[122-124] scanning microscope probe tips,[125] nanomechanical resonators,[126] and actuators.[127-129] Nanotubes can also be used as components in LED devices,[130] electrodes for batteries,[131] capacitors,[132] or devices that exploit field emission properties,[133-135] such as flat panel displays[136] and electron guns. Nanotubes also exhibit nonlinear optical properties,[137-141] which may be exploited, as

well. It has also been suggested that nanotubes may also be used as mechanical devices, such as nanotweezers, nanobearings, nanosprings, and nanooscillators.[142]

Nanotubes exhibit potential (and in some cases are already being used) in large-scale applications such as reinforcing filler and/or conductive filler. In such applications, the nanotubes are dispersed into a polymeric matrix. Such composites may be used for antistatic, or EM shielding purposes,[143,144] or applications requiring strength and resilience. The combination of antistatic and strength properties has been utilized in the automotive parts and computer components industries. The large surface area of the nanotubes gives rise to a whole host of other applications, such as gas sensors,[145-149] molecular pressure sensors,[118] actuators, gas storage, catalyst[150] and protein/DNA supports, Other uses include molecular-filtration membranes, [151] a template for fabricating nanowires both on the outside of the tube,[152] and the inside.[153,154]

2. Polymer-Nanotube Composites

As mentioned previously, carbon nanotubes exhibit a strong tendency to aggregate as a result of van der Waals forces. For a number of applications, the nanotubes must be dispersed in a polymeric matrix, thus the strong cohesive forces must be overcome. Much effort has been expended in determining effective methods for deaggregation. Effective deaggregation is critical for maximizing the effect of the nanotubes, whether the desired properties are reinforcing or conductive in nature; there are a number of literature reports of processes that overcome the van der Waals forces; deaggregation and dispersion is most often achieved by sonication[155-158] and/or high shear mixing[104,159] or extrusion.[160-162]

The sonication method is the most prevalent,[155,163] as it has been found that the cavitation forces and the resulting localized heating are effective in separating the tubes from each other. Unfortunately the cavitation forces have also been found to shorten[164] and severely degrade the tubes.[38] Several groups have undertaken studies in which the effect of sonication as a function of time or sonication frequency has been studied. In most cases, mild sonication conditions (low power, short time) performed in the presence of a surfactant,[165,166] or a solvent that exhibits some degree of interaction with the tubes appears to result in deaggregation, at least temporarily.[167,168] The composite is then prepared either by mixing the dispersion of the nanotubes with a polymer solution, or by polymerization in the nanotube dispersion (*in-situ* polymerization).

Extrusion and high shear mixing of nanotubes and polymer generate shear forces that can overcome the inter-tube van der Waals interactions,[58,104,160,162,169] effectively separating the tubes; the resulting dispersion can be stabilized to aggregation either by favourable polymer-nanotube interactions, or the presence of a surfactant. Some researchers employ a multi-step processing method, such as sonication followed by high-shear mixing.[159]

The functionalization of carbon nanotubes is well established in the literature; even large molecules, such as DNA[170,171] and polystyrene[172-174] have been tethered to the surface. The presence of functional groups on the nanotubes can enhance their processibility,[173] and their interaction with a polymeric matrix,[105,175-178] although functionalization is not required to ensure favourable interaction. In some applications, particularly where preservation of the electrical properties is critical, functionalization is undesirable as it results in disruption of the conjugated π-system,[179] thereby diminishing the properties that are highly dependent on this conjugation. Fortunately, favourable interactions between nanotubes and other species can be significant even in the absence of covalent bonding. Noncovalent interaction has been noted with various molecules, such as anthracene derivatives,[180] and even polymers, such as PPA,[138] PmPV,[181-186] PVP,[164,187] PSS,[164,187] PPE,[188] Triton,[189] and PEG.[190] In some cases, nanotube-polymer interactions, whose nature is believed to be π - π stacking, are strong enough to effect dispersion stabilization, and even solubilize the nanotubes. Computational studies indicate that there are three important polymer characteristics to effect nanotube solubilization: a backbone capable of twisting (therefore wrapping), π-conjugation to ensure favourable interaction, and solubilizing side groups.[191] Solubilization has been achieved with PPA,[138] PmPV,[181-186] PVP,[164,187] PSS,[164,187] and amylose,[192] which appear to wrap around the tube, although solubilization has also been accomplished without wrapping.[188] It has been

suggested that nanotubes may be effectively separated from amorphous carbon by the preferential interaction with polymers; the amorphous carbon can be removed by filtration, and nanotubes can be recovered through polymer unwrapping that occurs by changing the solvent system.[164,187] In some studies, the benefits of *in-situ* polymerization (versus post-polymerization mixing) were investigated and it would appear that in-situ polymerization leads to better interaction between the polymer and the nanotubes.[138,193]

2.1 Insulating Matrix Composites

A number of composites have been prepared in which the matrix polymer is chosen for its mechanical strength. The introduction of reinforcing filler in such a matrix often results in significant enhancement of the mechanical properties. The presence of the reinforcing filler can have two effects: firstly, assuming good matrix adhesion, load transfer can occur between the matrix and the filler, yielding a stronger composite; secondly, the presence of the filler can affect the matrix polymer at the interfacial region, for example, the degree of crystallinity, which ultimately affects the composite strength. When the filler is nano-size, a high proportion of the matrix is either at the interface or in close proximity to the interfacial region, thus a significant fraction of the matrix is affected by the presence of filler. As the properties of composites are attributed primarily to the interfacial region, it stands to reason that the better the dispersion, the greater the region of influence, and therefore the greater the effect of filler on the overall properties of the composite.[194]

In the absence of good matrix adhesion, the load applied to the composite will not result in load transfer but slippage, and there will be no reinforcing effect. Interfacial shear energy for van der Waals forces is approximately 3 orders of magnitude lower than when a chemical bond exists.[195] Mechanical studies of composites prepared with nanotubes functionalized to improve interfacial interaction indicate improvement in mechanical properties (*vide infra*), although high interfacial shear stress has been found to be significant between unfunctionalized nanotubes and PS and epoxy.[196] Mechanical testing of the composites yields information regarding the effect of the nanotubes. Raman spectroscopy, which measures the strain carried by the nanotubes, also provides insight into the effectiveness of load transfer.[28,113,197] In the case of MWNTs, results indicate that the load transfer occurs to a larger extent in compression versus tension.[28] Micro-Raman spectroscopy has been utilized in determining Young's modulus of nanotubes embedded in an epoxy matrix; frequency shifts in stress-sensitive bands yield information about the tensile and compressive stresses experienced by the nanotubes.[117] These stress-sensitive Raman-active bands are effective indicators of nanotube stress also caused by molecular pressure, which is exerted on the nanotubes when they are immersed in liquids.[118] In addition, dielectric spectroscopy has been utilized as a means of probing the dispersion of MWNTs in a matrix.[198]

There is much evidence in the literature that carbon nanotube/polymer composites exhibit superior mechanical properties over the polymeric matrix alone. Dispersing small amounts (usually up to 5 wt%) of nanotubes in PS,[155,199] PBO,[200] epoxy,[166] PVA,[201-204] PP,[104,169] PVK,[204] nylon-6,[205] HDPE,[190] polyimide,[206] PAA,[165] and ABS,[162] has been found to result in improvements in the mechanical properties. By exploiting the magnetic anisotropy of nanotubes, an aligned MWNT-polyester composite has also been prepared; this method is unique because it is done in a mold, as opposed to spinning which yields fibres or thin

films.[207] Electrospun fibers of polystyrene- and polyurethane-containing functionalized SWNTs exhibited increases in tensile strength and tangent modulus.[178] It has been reported that the preparation of nanotube-PMMA composites by *in-situ* radical polymerization yields covalent bonds between the nanotubes and the polymer; the AIBN initiator apparently reacts with the π-bonds of the nanotubes.[208]

If the electrical properties are of interest, then the existence of a conductive network, also known as an electrical percolating (or percolative) network, is crucial in order for dc electrical conduction to occur. Conductivity measurements give information about the percolation threshold, thus the conductive network. Dispersing nanotubes in insulating matrices has been a subject of great interest in the nanotube field, as the nanotube dimensions give rise to extraordinarily large aspect ratios (ratio of length to diameter). The high aspect ratios translate to low filler volumes required to achieve a conductive network. In fact, the use of nanotubes in place of carbon black yields conductive composites having a lower percolation threshold, and with a higher conductivity at the threshold.[58] Much effort has gone into the preparation of composites of varying insulating matrices, such as epoxy, [58,159,196] polypropylene,[104] ABS,[104,162] polystyrene,[104,155,193,196,207,209] PMMA,[157,210] poly(styrene-co-butyl acrylate),[211] PVA,[212] PC,[160] PC-PE blends.[161] The degree of dispersion, and therefore the conductive network is highly dependent on the processing method, and in many cases a percolation threshold of 1 wt %[160,161] or even lower has been achieved.[58,104,157,159] One investigation in particular has yielded a nanotube-epoxy composite exhibiting a percolation threshold of 0.0025 wt %, although this has been achieved by ensuring a non-homogeneous distribution of nanotubes.[58] An excellent dispersion of SWNTs in polystyrene has been achieved by mixing an aqueous polystyrene latex solution with an aqueous dispersion of SDS and SWNTs, followed by freeze-drying and molding into a film. The resulting film exhibits a percolation threshold of 0.28 wt % nanotubes.[213]

In several cases, both the electrical and mechanical properties of the composites have been determined, and some studies have shown that even the small amounts of nanotubes required to achieve a conductive network are sufficient to also enhance the mechanical integrity.[155,160,161,211,212] In addition to imparting electrical conductivity and strength to a composite, the nanotubes have also been found to enhance the stability of the composite. The nanotubes are believed to exhibit antioxidant properties,[214] as well as improve the thermal stability of the composite.[158,211,212,215]

2.2 Conducting Polymer Composites

A number of researchers have prepared and characterized carbon nanotube – conducting polymer (NT-CP) composites. NT-CP composites are particularly interesting, as they have been found to exhibit unique properties, likely due to electronic interaction between the components. Indeed, there is evidence for enhanced electrical properties, and a number of applications have been cited, such as capacitors,[216,217] actuators,[218] Schottky diodes,[215] electrodes,[219] nanowires for optoelectronic applications,[220] and organic light emitting diodes (OLEDs).[130,221,222] Both conducting polymers and carbon nanotubes possess conjugated π-systems and the nature of any electronic interaction is proposed to occur via π-π stacking. Composites with a number of conducting polymers, such as polyaniline and derivatives, [215,223-

[233] polypyrrole,[131,132,234-236] polythiophene derivatives,[237] and polyacetylene,[229] have been prepared and characterized.

Polyaniline – nanotube composites have been prepared by *in-situ* chemical oxidative polymerization,[223-227,230-232] *in-situ* electropolymerization,[228] and *ex-situ* mixing.[215,229] Evidence for electrical interaction, in the form of conductivity enhancement, was observed in several *in-situ* polymerization studies, [223,224,226] but not in the *ex-situ* polymerization,[229] thus it would appear that the *in-situ* prepared composites possess enhanced polymer – nanotube interactions. In one study, both *in-situ* and *ex-situ* polymerization methods were employed, and it was found that the *in-situ* polymerization conditions caused fragmentation of the nanotubes.[233]

Polypyrrole – nanotube composites have been prepared by electropolymerization in the presence of aligned nanotubes that functioned as the working electrode. This process resulted in the formation of polypyrrole-coated nanotubes, in which the coating forms more quickly and uniformly compared to flat metal substrates,[131,234] and exhibit high charge capacity. Comparison with flat metal substrates indicated improved electrochemical redox performance.[131] The composite films retained their capacitive characteristics well beyond polymerization charges that degenerate pure polypyrrole films, and exhibited much larger CV peak currents relative to polypyrrole films, suggesting superior capacitance performance.[132] These coated nanotubes may find use as capacitors and high performance electrodes in rechargeable batteries. Polypyrrole – nanotube composites have also been prepared electrochemically in which the nanotubes are acid-functionalized and act as the supporting electrolyte, and thus the dopant. The nanotubes become embedded in the polypyrrole film, and high resolution electron microscopy (HREM) reveals polypyrrole bridges between polypyrrole-coated nanotubes.[238] Although the preferred method of polypyrrole fabrication is that of electropolymerization, there is a report of chemical oxidative polymerization in the presence of nanotubes; the nanotubes were uniformly coated with polypyrrole, however, the composite conductivity did not exceed that of the nanotubes alone, leading to the conclusion that there was no electronic interaction.[235]

Polythiophene-MWNTs nanocomposites have recently been reported, in which poly(2-hydroxyethyl)thiophene is tethered to the nanotubes by ester linkages.[237] The nanocomposite prepared in this fashion, exhibited higher conductivity than that prepared by post-polymerization mixing; the authors did not report any *in-situ* polymerization results.

Some researchers claim that the electrical property enhancement is a result of the nanotubes doping the conducting polymers,[226,239] while others found that the nanotubes doped polyacetylene, but not polyaniline (both were initially undoped), under the same conditions.[229] Another interesting study indicates that sulfonated nanotubes can both dope polyaniline as well as provide a template for polymerization.[240]

3. Summary

Although carbon nanotubes were discovered over a decade ago, progress in many areas of characterization and applications was initially hindered by the high cost of production, as well as the requirement of processing the nanotubes. In recent years, the production costs have decreased dramatically as a result of the development of new, high-throughput commercial processes that yield high quality nanotubes, and it is speculated that nanotube production costs will continue to drop. Furthermore, many processing methods have been developed, and are continually being improved upon, in order to fully exploit the extraordinary properties. Hence, progress in the field of polymer-nanotube composites is rapid with the availability of relatively cheap starting materials, and advancements in non-destructive processing methods.

The number of applications for which polymer-nanotube composites may be used is large, and widely varied, ranging from small electronic devices to large structures strong enough to replace steel, and the applications will continue to expand as the cost and production issues continue to decrease. The use of polymer-nanotube composites will become much more prevalent in the foreseeable future, both in civilian and military situations. As mentioned previously, military applications include electromagnetic shielding and absorption, frequency-selective coatings, antistatic devices, high-strength low-density corrosion-resistant components, lightweight energy storage, electronic devices, transducers, sensors (chemical and pressure), and nonlinear materials (for electro-optical warfare).

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List of symbols/abbreviations/acronyms/initialisms

a_1, a_2	hexagonal lattice unit vectors
$a_{c\text{-}c}$	nearest neighbour carbon-carbon distance in graphite
AIBN	2,2'-azobisisobutyronitrile
ABS	acrylonitrile-butadiene-styrene
BET	Brunauer-Emmett-Teller
c_1	lowest energy van Hove singularity in conduction band
C_h	chiral vector
cm^{-1}	wavenumber
CP	conducting polymer
CV	cyclic voltammetry
CVD	chemical vapour deposition
d_t	nanotube diameter
DNA	deoxyribonucleic acid
DND	Department of National Defence
DOS	density of states
DRDC	Defence R & D Canada
DWNT(s)	double-walled carbon nanotube(s)
E^{M}_{gap}	band gap of metallic nanotube
E^{S}_{gap}	band gap of semiconducting nanotube
EM	electromagnetic

eV	electronvolts (energy units)
γ_o	tight binding overlap energy
GHz	Gigahertz (frequency units)
HDPE	high density polyethylene
HFCVD	hot filament-assisted chemical vapour deposition
HiPco	high-pressure carbon monoxide pyrolysis
HREM	high resolution electron microscopy
HWCVD	hot wire chemical vapour deposition
MPCVD	microwave plasma chemical vapour deposition
MWNT(s)	multi-walled carbon nanotube(s)
m^2/g	square meters per gram, unit of surface area
(n, m)	lattice indices
NIR	near infrared, region in electromagnetic spectrum
nm	nanometer, unit of length
NT	nanotube
OLED(s)	organic light emitting diode(s)
PAA	polyacrylic acid
PBO	poly(p-phenylene benzobisoxazole)
PC	polycarbonate
PE	polyethylene
PECVD	plasma enhanced chemical vapour deposition
PEG	polyethylene glycol
PMMA	polymethylmethacrylate
PmPV	poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene)

PP	polypropylene
PPA	poly(phenyl acetylene)
PPE	poly(aryleneethynylene)
PS	polystyrene
PSS	polstyrenesulfonate
PVA	poly(vinyl alcohol)
PVK	poly(9-vinyl carbazole)
PVP	polyvinylpyrrolidinone
ρ	density
RBM	radial breathing mode
redox	reduction oxidation
RTCVD	rapid thermal chemical vapour deposition
SDS	sodium dodecylsulfate
SEM	scanning electron microscopy
STM	scanning tunnelling microscopy
SWNT(s)	single-walled carbon nanotube(s)
θ	chiral angle
TEM	transmission electron microscopy
TPa	Terapascals, pressure unit
v_1	highest energy van Hove singularity in valence band
W/m·K	Watts per meter per Kelvin, thermal conductance units
wt %	percent by weight

Glossary

Technical term	Explanation of term
allotrope[‡]	a structurally different form of an element
fullerene[‡]	a form of carbon having a large spheroidal molecule consisting of an empty cage of sixty or more carbon atoms
functionalization	the introduction of functional groups (atom or groups of atoms that provide a molecule with a reactive site)[†]
graphene	a single layer of graphite
Young's modulus[‡]	a coefficient of elasticity applicable to the stretching of a wire

‡ www.hyperdictionary.com

† Radel, S. R.; Navidi, M. H. *Chemistry*; Second ed.; West Publishing Company: New York, 1994.

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Carbon nanotubes were first discovered in 1991, and quickly became the focus of much research activity, due to their exceptional electrical, mechanical, and thermal properties. The extraordinary properties arise from the unique tubular structure; the nanotubes may be envisioned as rolled up graphene sheets that are on the order of a nanometer in diameter, and microns in length, resulting in high aspect ratios (length/diameter). In addition to the many applications of pure carbon nanotubes (gas storage, sensors, electronic devices, electron microscope tips, and electron emission devices), there are also a number of applications in which the nanotubes are dispersed in a polymeric matrix, such as electromagnetic shielding, antistatic coatings, high-strength low-density corrosion-resistant components, and lightweight energy storage. The presence of small amounts of nanotubes in an insulating polymeric matrix has been found to improve the mechanical properties as well as render the composite electrically conductive, thus polymer-carbon nanotube composites are of interest primarily for their mechanical and electrical properties. When the matrix polymer is also electrically conductive, in many cases the composite exhibits enhanced electrical properties. This technical memorandum is a survey of current literature on both insulating and conductive polymer – carbon nanotube composites.

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